



ENTHALPY OF FORMATION OF $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\text{OCOCCL}_3)_2$

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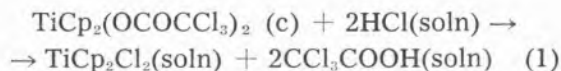
While the question "What are the systematics of the metal-ligand bond energies in organometallic compounds?" was considered fundamental in an area recently proposed as being of top priority in the USA [1], relatively little work is currently being done worldwide on the thermochemistry of this class of compounds. Such work is, in our view, an essential part in answering that question.

We have been determining the enthalpies of formation and bond enthalpy contributions in a series of organometallic compounds of general type MCp_2L_2 (M = transition metal; $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; L = ligand). In particular for $\text{M} = \text{Ti}$ and L = oxygen donor atom ligand we have previously reported the results of our studies on compounds $\text{TiCp}_2(\text{OR})_2$ ($\text{R} = \text{C}_6\text{H}_5$, $2\text{-CH}_3\text{C}_6\text{H}_4$, $3\text{-CH}_3\text{C}_6\text{H}_4$, $4\text{-CH}_3\text{C}_6\text{H}_4$, $2\text{-ClC}_6\text{H}_4$) [2] and $\text{TiCp}_2(\text{OCOR})_2$ ($\text{R} = \text{C}_6\text{H}_5$ and CF_3) [3], aiming to investigate the influence of the group R in the titanium-oxygen bond strength. The results obtained for the bond enthalpy terms, $E(\text{Ti-O})$, and the mean bond dissociation enthalpies, $\bar{D}(\text{Ti-O})$, suggest that the titanium-oxygen bond strength is fairly insensitive to the nature and position of group R . In this note we report thermochemical data related to the complex $\text{TiCp}_2(\text{OCOCCL}_3)_2$.

The reaction and solution enthalpies were measured in the reaction-solution calorimeter previously described [4]. The thermochemical measurements were not made under nitrogen, since the compound studied is not affected by exposure to air or moisture for short periods. However, trichloroacetic acid (Carlo Erba) was purified by sublimation and always handled under nitrogen due to its hygroscopic character. $\text{TiCp}_2(\text{OCOCCL}_3)_2$ was also prepared under nitrogen atmosphere and using Schlenk tube techniques, by reacting TiCp_2Cl_2 with NaOCOCCL_3 in stoichiometric amounts, in dichloromethane. After refluxing for two hours, the reaction mixture was filtered and crystals were obtained by slow removal of the solvent. The orange product was washed with diethyl ether and recrystallized twice from benzene. The solution

used in the thermochemical studies was prepared from Merck p. a. hydrochloric acid and acetone (which were used without any further purification).

Thermochemical measurements on reaction (1),



were used as the main source of data to derive bond-enthalpy contributions. The solvent for this reaction was a 1:4 mixture of 10.0 mol dm⁻³ aqueous hydrochloric acid and acetone [3]. Reaction (1) was found to be fast and quantitative and its products were confirmed by i. r. spectroscopic analysis.

The reaction and solution enthalpies presented below are mean values from at least five independent experiments and are referred to 298.15 K. The associated uncertainties are twice the standard deviations of those means. As auxiliary data, the following standard enthalpies of formation and enthalpies of sublimation at 298.15 K were used in evaluating the thermochemical results: $\Delta H_f^\circ(\text{HCl}, \text{soln}) = -172.59 \pm 0.51 \text{ kJ.mol}^{-1}$ [3]; $\Delta H_f^\circ(\text{CCl}_3\text{COOH}, \text{c}) = -503.3 \pm 8.4 \text{ kJ.mol}^{-1}$ [5]; $\Delta H_f^\circ(\text{TiCp}_2\text{Cl}_2, \text{c}) = -383.2 \pm 7.9 \text{ kJ.mol}^{-1}$ [6]; $\Delta H_s^\circ(\text{CCl}_3\text{COOH}) = 75.0 \pm 0.3 \text{ kJ.mol}^{-1}$ (determined by Calvet microcalorimetry) [7]; $\Delta H_s^\circ(\text{TiCp}_2\text{Cl}_2) = 118.8 \pm 2.1 \text{ kJ.mol}^{-1}$ [6]; $\Delta H_f^\circ(\text{Cl}, \text{g}) = 121.302 \pm 0.008 \text{ kJ.mol}^{-1}$ [8]; $\Delta H_f^\circ(\text{H}, \text{g}) = 217.997 \pm 0.006 \text{ kJ.mol}^{-1}$ [8]. The thermochemical results obtained are $\Delta H_r = 26.4 \pm 1.4 \text{ kJ.mol}^{-1}$ (enthalpy of reaction (1)), $\Delta H_{d1} = 16.3 \pm 1.3 \text{ kJ.mol}^{-1}$ (enthalpy of solution of $\text{TiCp}_2\text{Cl}_2(\text{c})$ in the mixture of aqueous HCl and acetone plus stoichiometric amounts of CCl_3COOH), $\Delta H_{d2} = -4.02 \pm 0.26 \text{ kJ.mol}^{-1}$ (enthalpy of solution of CCl_3COOH in the reaction mixture) and $\Delta H_{d4} = -3.66 \pm 0.15 \text{ kJ.mol}^{-1}$ (enthalpy of solution of H_2O in the reaction mixture). These values and the auxiliary data given above yield $\Delta H_f^\circ[\text{TiCp}_2(\text{OCOCCL}_3)_2, \text{c}] = -1095.0 \pm 18.6 \text{ kJ.mol}^{-1}$. The enthalpy of sublimation of the

complex is estimated as $130 \pm 8 \text{ kJ.mol}^{-1}$, leading to $\Delta H_f^\circ[\text{TiCp}_2(\text{OCOCCL}_3)_2, \text{g}] = -965.0 \pm 20.2 \text{ kJ.mol}^{-1}$.

The titanium-oxygen mean bond dissociation enthalpy $\overline{D}(\text{Ti-O})$ and the bond enthalpy term $E(\text{Ti-O})$ in the complex $\text{TiCp}_2(\text{OCOCCL}_3)_2$ can be obtained through equations (2) and (3), respectively, as discussed in previous papers [2,9]:

$$\begin{aligned} \overline{D}(\text{Ti-O}) = & E(\text{Ti-Cl}) + \Delta H_f^\circ(\text{CCl}_3\text{COO}, \text{g}) - \\ & - \Delta H_f^\circ(\text{Cl}, \text{g}) - \Delta H_f^\circ[\text{TiCp}_2(\text{OCOCCL}_3)_2, \text{g}] - \\ & - \Delta H_f^\circ(\text{TiCp}_2\text{Cl}_2, \text{g}) / 2 + ER_3 / 2 \quad (2) \end{aligned}$$

$$\begin{aligned} E(\text{Ti-O}) = & E(\text{Ti-Cl}) + \Delta H_f^\circ(\text{CCl}_3\text{COO}^*, \text{g}) - \\ & - \Delta H_f^\circ(\text{Cl}, \text{g}) - \Delta H_f^\circ[\text{TiCp}_2(\text{OCOCCL}_3)_2, \text{g}] - \\ & - \Delta H_f^\circ(\text{TiCp}_2\text{Cl}_2, \text{g}) / 2 + (ER_3 - ER_1) / 2 \quad (3) \end{aligned}$$

CCl_3COO^* is the unreorganized ligand and ER_3 and ER_1 are the reorganization enthalpies of the fragments TiCp_2 from the dichloride complex and from $\text{TiCp}_2(\text{OCOCCL}_3)_2$, respectively. ER_3 was calculated as ca. -10 kJ.mol^{-1} , by using extended Hückel molecular orbital calculations [10]. ER_1 cannot be evaluated since the structure of the complex has not been determined. However, considering that compounds TiCp_2L_2 have very similar structural parameters [9, 11] and assuming that the Cp-Ti-Cp angles in $\text{TiCp}_2(\text{OCOCCL}_3)_2$ and in $\text{TiCp}_2(\text{OCOC}_6\text{H}_5)_2$ [12] are similar, then $ER_1 \approx -8 \text{ kJ.mol}^{-1}$, which makes the correction terms negligible ($ER_3 - ER_1 \approx -1 \text{ kJ.mol}^{-1}$). Another usual assumption to be considered here is that structures of L in LH and in complexes MCp_2L_2 are comparable [2, 9], so that $\Delta H_f^\circ(\text{L}^*, \text{g})$ can be obtained through the Laidler term $E(\text{O-H}) = 451 \pm 8 \text{ kJ.mol}^{-1}$ [13]. An experimental value for $D(\text{CCl}_3\text{COO-H})$ is not available. Studies on the effects of halogen substituents on the intrinsic acidity of carboxylic acids determined by measurements of gas-phase ion equilibria showed that the introduction of a halogen substituent leads to a large increase of acidity [14, 15]. However, it is generally accepted that $D(\text{RCOO-H})$

is not very dependent on the nature of R [14]. So we have assumed that $\text{D}(\text{CCl}_3\text{COO-H}) \approx \text{D}(\text{CH}_3\text{COO-H}) = 433 \pm 10 \text{ kJ.mol}^{-1}$ [16]*. The calculated $\overline{\text{D}}(\text{Ti-O})$ and $\text{E}(\text{Ti-O})$ results in the complex $\text{TiCp}_2(\text{OCOCCL}_3)_2$ are shown in Table 1, together with the equivalent bond enthalpies for the benzoate and trifluoroacetate complexes [3], corrected for ΔH_{d4} . These values rely on $\text{E}(\text{Ti-Cl}) = 430.5 \pm 1.3 \text{ kJ.mol}^{-1}$ [2, 6, 9].

Table 1 *

Complex	$\overline{\text{D}}(\text{Ti-O}) / \text{kJ.mol}^{-1}$	$\text{E}(\text{Ti-O}) / \text{kJ.mol}^{-1}$
$\text{TiCp}_2(\text{OCOCCL}_3)_2$	446 ± 11	464 ± 9
$\text{TiCp}_2(\text{OCOCF}_3)_2$	433 ± 11	451 ± 9
$\text{TiCp}_2(\text{OCOC}_6\text{H}_5)_2$	440 ± 6	455 ± 9

* Values do not include $\text{ER}_3/2$ and $(\text{ER}_3\text{-ER}_1)/2$ corrections.

The results support our conclusion that titanium-oxygen "bond strengths" in compounds of type $\text{TiCp}_2(\text{OCOR})_2$ are not greatly affected by the nature of group R. Furthermore, the determined values of $\text{E}(\text{Ti-O})$ in these complexes are comparable with $\text{E}(\text{Ti-O})$ in the series of complexes $\text{TiCp}_2(\text{OR})_2$ ($430\text{--}462 \text{ kJ.mol}^{-1}$) [2]. Finally, a mean value $\overline{\text{E}}(\text{Ti-O}) = 452 \pm 16 \text{ kJ.mol}^{-1}$ in organometallic compounds of the type TiCp_2L_2 is not far from the reported $\overline{\text{E}}(\text{Ti-O}) = 466 \pm 15 \text{ kJ.mol}^{-1}$ in $\text{Ti}(\text{OR})_4$ compounds ($\text{R} = \text{C}_2\text{H}_5$, $\text{n-C}_3\text{H}_7$, $\text{i-C}_3\text{H}_7$, $\text{n-C}_4\text{H}_9$, $\text{i-C}_4\text{H}_9$, $\text{sec-C}_4\text{H}_9$, $\text{ter-C}_4\text{H}_9$, $\text{n-C}_5\text{H}_{11}$, $\text{ter-C}_5\text{H}_{11}$, [11, 17, 18].

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* The reported results for $\text{D}(\text{CH}_3\text{COO-H})$ cover a wide range of values. The use of a "high" value for $\text{D}(\text{CH}_3\text{COO-H})$, ca. $443 \pm 8 \text{ kJ.mol}^{-1}$ [D.F. McMillen and D.M. Golden, *Ann. Rev. Phys. Chem.*, **33**, 493 (1982)] would yield larger values in Table 1.

measuring the enthalpy of sublimation of trichloroacetic acid. Thanks are due to the Junta Nacional de Investigação Científica e Tecnológica and to the Instituto Nacional de Investigação Científica for financing this work. M.S.S. thanks Laboratório Nacional de Engenharia e Tecnologia Industrial for granting her leave of absence to participate in this project.

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